Evaluating strategies for catalytic upgrading of pyrolysis oil in liquid phase

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ABSTRACT

Upgrading of pyrolysis oil from biomass offers great potential economic and environmental benefits for the production of sustainable and renewable energy sources. Meanwhile, challenges remain in the development of technical- and cost-effective catalysts and operating processes. One promising approach is liquid phase upgrading, which exhibits numerous benefits. This paper reviews recent progress and future possibilities for obtaining fuels from biomass using this approach. Key upgrading reactions for different oxygenated compounds in pyrolysis oil, including ketonization, aldol condensation, alkylation, hydrodeoxygenation, and oxygenation are discussed. Development of effective catalysts and efficient integration of multiple consecutive reaction steps in one single reactor make liquid phase upgrading competitively advantageous.

1. Introduction

In recent years, utilization of biomass in the energy sector has attracted renewed interest across the world. While the output of other renewable sources is primarily electricity, biomass is able to produce liquid, gaseous, or solids of variable energy contents [1–5]. Among the different biomass conversion processes investigated in the last few decades, fast pyrolysis coupled with catalytic upgrading is one of the most attractive processes both economically and technologically [6–11]. Fast pyrolysis is a thermochemical conversion method in which the biomass feedstock is heated at high temperatures (500–800 °C) for a short period of time (<2 s) in the absence of air [11]. The vapors formed during pyrolysis condense into liquid products (so-called bio-oil). High yields of bio-oil are typically obtained, but the inherent characteristics of the product, including high viscosity, chemical instability, high corrosivity and incompatibility with conventional fuels, render it useless as a fuel. Stabilization can be accomplished by oxygen removal from the abundant oxygenated compounds present in the product, which include acids, aldehydes, esters, phenolics, furanics and oxygenated oligomers [12,13]. The production of stabilized bio-oils has received increasing attention in the pursuit of economically viable large-scale biomass conversion processes [14].

The various possibilities for stabilization of bio-oil proposed in the literature can be divided into four general strategies. The first one is to directly contact the vapor exiting the pyrolysis reactor with a catalyst before its condensation. This strategy, which has been under extensive study in recent years [15,16], has the advantage of preventing some of the polymerization and gum formation reactions that occur in liquid phase and greatly reduce viscosity and instability of bio-oil. The processes that have been investigated with this strategy include suitable catalysts that either deoxygenate the oxygenated compounds or utilize the oxygen functionalities to facilitate the formation of C—C bonds, for example, via ketonization of carboxylic acids or aldol condensation of aldehydes and ketones [17–22].

A second strategy that has been widely proposed since early 1980s is hydrotreating, which includes two options: (i) hydrotreating after condensation of bio-oil [23–27] and (ii) high-pressure post-pyrolysis hydrotreating integrated with a hydropyrolysis reactor [28].

In the former case, the pyrolysis vapors are first condensed and the liquid bio-oil is then transferred and treated in conventional hydrotreating units using commercial catalysts such as sulfided Co—Mo and Ni—Mo, similar to those employed in oil refineries. However, it was found that the low chemical and thermal stability of bio-oil make it unprocessable at high temperatures typically used in conventional hydrotreating units. In addition, the hydrogen consumption becomes exceedingly high. For example, when bio-oil from a poplar wood was hydrotreated over a sulfided Co—Mo catalyst at 355 °C and 13.8 MPa, the liquid product contained about 5% oxygen, but the yield was only 23% [25]. More importantly, coke formation and rapid catalyst deactivation is a common problem found in hydrotreating of bio-oils. Therefore, an additional pre-hydrogenation deoxygenation (HDO) step at moderate temperatures is required to stabilize the bio-oil, in which the most reactive groups are converted to less active ones to avoid severe

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coking in a subsequent step. The same catalysts such as sulfided Co—Mo or Ni—Mo have been used for both steps. It has been reported that this two-step process could produce yields up to 0.53 L refined-oil/L oil feed. However, almost half of this yield is composed of light alkanes, which probably arise from the small oxygenates (C1–C5) in the original bio-oil [24,25]. Over the last 25 years, much research has been carried out to develop more active and stable catalysts as well as to optimize reactor set-up for hydrotreating process and many progresses have been made. However, the large amount of hydrogen required and a substantial amount of carbon loss in light alkane products has impeded its commercialization.

The second option of this strategy is to conduct biomass pyrolysis under medium hydrogen pressure (20–35 bar) in a catalytic fluidized bed (so-called hydropyrolysis reactor) directly connected to a hydrotreating unit, which can further perform hydrodeoxygenation of liquid products and produce hydrogen by reforming some of the light gases obtained from hydropyrolysis [28]. This process has been shown to produce liquid oil with less than 2.2 wt% oxygen from a variety of biofeeds including bagasse, corn stover, algae and wood. However, the added complexity and risk of operating the pyrolysis unit under hydrogen does not result in improved liquid yield (>C5). Therefore, the loss of liquid yield remains as a major challenge for the hydrotreating approach.

A third strategy for biofuel production is co-processing pre-hydrogenated pyrolysis oil together with petroleum feedstocks in conventional petroleum refining units, such as fluidized catalytic cracking (FCC) and hydrotreating [29–33]. The obvious advantage of this approach is the reduced capital costs of utilizing existing refinery infrastructure and avoiding construction of new units exclusively dedicated to biomass processing. To elucidate the possibilities of co-processing approach, some studies have been conducted by co-feeding model oxygenated compounds and hydrocarbon feeds into FCC. For example, Lappas et al. [29] combined hydrodeoxygenation and co-processing in a FCC unit of a mixture of pyrolysis oil with vacuum gas oil (VGO). Before mixing it with VGO, the pyrolysis oil was hydrotreated. In comparison with VGO, the co-processing with pyrolysis oil resulted in higher coke production (0.5 wt%), lower liquid petroleum gas, and increased selectivity toward aromatics. In another study, Corma et al. [33] investigated the catalytic cracking of model bio-oil oxygenates such as glycerol and sorbitol mixed with VGO over different cracking catalysts to elucidate the main reaction pathways and the effect of cofeeding oxygenates. They pointed out that the catalytic cracking of oxygenates involves a complex reaction network. Gas phase products consisting of olefins, CO, CO$_2$, H$_2$, and paraffins are produced by dehydration, steam reforming, water gas shift, decarbonylation, and dehydrogenation/hydrogenation reactions. Aromatics are formed by condensation and Diels–Alder reactions of olefins and dehydrated species. Among those catalysts tested, ZSM-5 produced lower level of cokes and high amount of aromatics and olefins. The other catalysts investigated, i.e., a commercial FCC catalyst containing Y-zeolite and silica–alumina matrix, a commercial FCC catalyst with V and Ni impurities (ECAT), Al$_2$O$_3$, and pure HY produced high amounts of coke and low amounts of aromatics and olefins. Addition of oxygenated compounds to VGO did not significantly change the product distribution of the final products as compared with VGO alone. However, bio-oil compounds decreased the gasoline yield and overall conversion, increased the coke amount and the olefin to paraffin ratio of C2–C4 hydrocarbons. On the other hand, Bui et al. [31] studied the co-processing of bio-oil and petroleum model compounds under hydrodesulfurization conditions. Similar to the case of the catalytic cracking studies, decreased catalyst performance was observed at the relatively low temperature and high contact time used in the study. This decreased activity might be due to intermediate phenols competing with sulfur-containing molecules for hydrogenation sites. It is clear that while co-processing might be a promising route with great economical advantages, it presents serious challenges, including efficiency of the process and catalyst development, which require further investigation.

A fourth alternative for bio-oil upgrading that would avoid some of the problems associated with the above three strategies is to conduct catalytic conversion in liquid phase over pre-fractionated segments of bio-oil. This review will concentrate on this upgrading strategy. After condensation, the full bio-oil cannot be fractionated by conventional distillation since reheating this unstable liquid results in undesirable oligomerization reactions. However, there are different ways of accomplishing fractionation of the bio-oil during condensation, without the need to reheat it. One of them is to conduct the thermochemical conversion in stages. For example, one can conduct sequential heating treatments at increasing temperatures [34–38], which can thermally break down biomass components (hemicellulose, cellulose, lignin) at incremental temperature due to increased thermochemical stability. Initial heating at temperatures below 300 °C (first torrefaction) results in evolution of small oxygenates (primarily acetic acid and acetol) and water decomposed from hemicellulose. Subsequent heating to 400 °C leads to breaking down of cellulose producing mainly levoglucosan and hydroxymethyl furfural (HMF) [38]. In the final, fast-pyrolysis step (~550 °C), The more stable lignin fraction is decomposed, forming mostly phenolic compounds.

In this contribution, we will discuss current upgrading approaches and future possibilities for bio-oils involving this new strategy. Fig. 1 depicts the simplified approach for bio-oil upgrading in liquid phase. After a multi-stage pyrolysis of lignocellulosic biomass at different temperatures and reaction time the liquid product can be separated into light, medium and heavy oxygenate components. Therefore, the product mixtures from different stages can be selectively upgraded in liquid phase by different catalysts via different reaction approaches. Alternatively, the fractionation of bio-oil can be done during the condensation of the vapors [39]. Either of the two options enhances the upgrading process greatly since it reduces the complexity of the problem from dealing with a variety of different chemistries simultaneously to a series of simpler problems in tandem. While the hydrotreating approach treats the entire bio-oil as a common system, in this case, with a preceding fractionation, one can attack different fractions differently. Specifically, as illustrated in Fig. 1, from different bio-oil fractions one could: (i) partially remove unstable oxygen functional groups, (ii) couple C—C bonds to elongate the carbon chain and (iii) completely remove the remaining oxygen functionality. The light oxygenates, consisting of water-soluble compounds such as acetic acid, acetol, acetaldehyde, etc. can undergo condensation reactions to reduce acidity and partially remove oxygen. For example, ketonization of acetic acid (or even acetol) produces acetone, an attractive building block that can be further coupled with sugar derived compounds, such as furfurals [40]. Ketones can also be hydrogenated to alcohols, which in turn can be used as alkylating agents of phenolic compounds, via acid-catalyzed alkylation [41]. These products, with enlarged C-chain length, can undergo hydrodeoxygenation to produce long chain hydrocarbons, with minimum loss in liquid yield. The sugar derived compounds can either couple with acetone as mentioned above, or undergo oxidation to produce acids, which can also be ketonized and further upgraded as discussed above. The phenolics from lignin fraction of biomass (heavy products) can be alkylated with light alcohols or can undergo direct hydrodeoxygenation. The purpose of this review is to summarize the recent progress in liquid phase bio-oil upgrading and discuss some promising upgrading approaches.
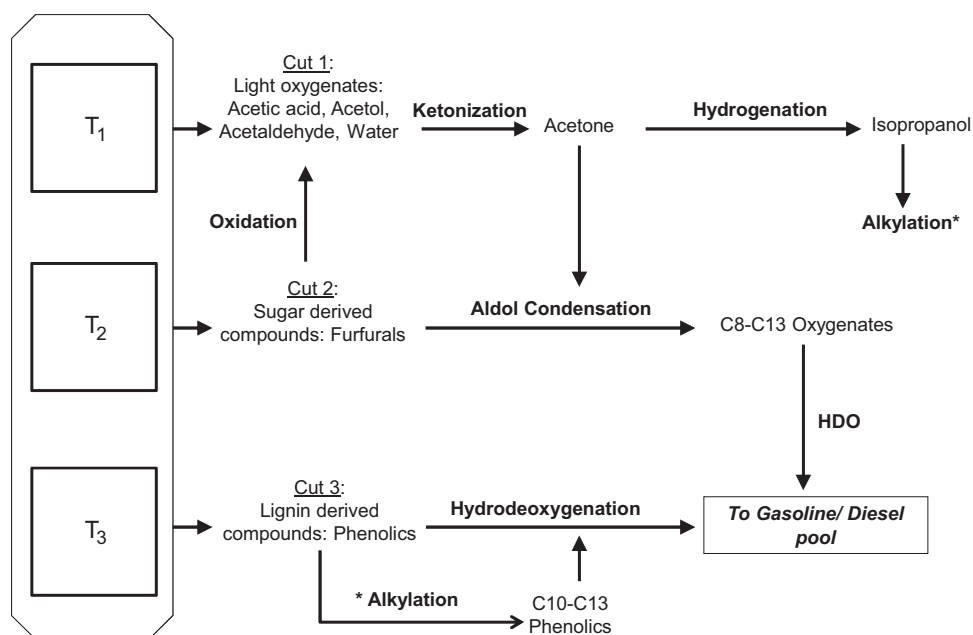
Fig. 1. Process concept: liquid phase catalytic cascade connected to a multi-stage pyrolysis.

2. Conversion of light oxygenates

In the proposed upgrading strategy it is crucial that the fraction of light-oxygenates (i.e., small acids and aldehydes) undergo C—C bond coupling to produce larger oxygenates, which can subsequently be hydrodeoxygenated to fuel-range hydrocarbons.

The low-temperature torrefaction produces large amounts of water along with water-soluble small oxygenates. For this fraction, aqueous-phase upgrading is highly desirable. In this section, we present recent progress in aqueous-phase ketonization of small acids and discuss the possibilities of combining hydrogenation and alkylation to incorporate small oxygenates into phenolics.

2.1. Ketonization of small carboxylic acids

One of the first steps in bio-oil upgrading is the removal of acids. Small acid compounds such as acetic acid and propanoic acid not only bring corrosion problems to any process, but also greatly reduce the stability of bio-oil. Acetic acid is one of the most abundant single components in bio-oil. For example, the bio-oil produced from sawdust contains about 10% acetic acid [42]. In ketonization reaction, two carboxylic acid molecules couple to produce a larger ketone molecule eliminating CO_2 and H_2O. The ketones thus produced can undergo further C—C coupling via aldol-condensation to increase C chain length or hydrogenation to alcohol followed by alkylation as illustrated in Fig. 1.

As an example, we discuss here the conversion of acetic acid to acetone in aqueous-phase, which is a desirable process when the fraction containing acetic acid is in aqueous phase. Vapor-phase ketonization of acetic acid on oxides has been extensively studied in the past [43–50,17,51–53]. It is well known that metal oxides, such as TiO_2, ZrO_2 and CeO_2 possess high ketonization activity and selectivity to acetone. Also, it is known that the addition of catalytic metals with high hydrogen dissociation activity, such as Pd, Pt, Rh and Co, significantly improves the reducibility of the metal oxides and consequently their ketonization activity [51,53]. Density functional theory (DFT) studies [54] have shown that doping TiO_2 anatase with Au or Fe weakens the M—O bonds around the dopants and reduces the energy required to form a defect site O vacancy from 2.7 eV in pure TiO_2 to 1.24 eV in

Fe-doped catalyst. Dooley et al. [51] studied the effects of adding Co and Pd to alumina-supported CeO_2 particles in vapor phase ketonization of isobutyric, acetic, and decanoic acids. By using X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS), they showed that, upon the incorporation of small amounts of Pd and Co to the base CeO_2/Al_2O_3 oxides, a significant enhancement in the number of oxygen vacancies occurs, which increases the ketonization activity of the oxides.

The challenge is to find an active material that can catalyze ketonization reaction in aqueous phase at moderate temperatures in order to minimize decomposition and re-polymerization of other bio-oil components. Study on aqueous phase ketonization using metal oxide catalysts is still very limited to date. The presence of water in high concentrations lowers the activity of the oxide due to competitive adsorption and active site blocking.

Aqueous-phase feeds of pentanoic acid derived from levulinic acids have been converted at 350 °C to ketones over 0.1%Pd/Nb_2O_5 and $Ce_{0.5}Zr_{0.5}O_2$ catalysts [55]. In the first step, levulinic acid was hydrogenated over non-acidic catalysts Ru/C to produce Ƴ-valerolactone, which in turn transformed to pentanoic acid by means of ring opening on the acid site Nb_2O_5 and hydrogenation on Pd sites. The intermediate pentanoic acid was then ketonized to form 5-nonanone. The results indicated that levulinic acid can be completely converted and the 5-nonanone yield can reach 60% over Pd/Nb_2O_5 in a single reactor. The yields can be increased to almost 90% by using a dual-catalyst approach with Pd/Nb_2O_5 + $Ce_{0.5}Zr_{0.5}O_2$ in a cascade approach. This study demonstrated the great potential for ketonization of carboxylic acid in the presence of water phase. However, the high temperatures used may not be adaptable for upgrading the bio-oil acid fractions.

In a recent study, Pham et al. [56] compared the ketonization activity of acetic acid in aqueous environment over TiO_2, Ru/TiO_2, Ru/activated carbon, TiO_2/activated carbon, and Ru/TiO_2/activated carbon at a mild temperature of 180 °C. They found that while Ru does not impart any significant ketonization activity and TiO_2 alone shows poor activity, the addition of Ru to TiO_2 results in significant activity at low temperatures. That is, the conversion of the catalysts containing both Ru and TiO_2 is at least twice that of TiO_2. XPS and TPR characterizations of the catalysts also confirmed strong

Table 1
Comparison of catalytic activity among Ru/C, TiO$_2$/C, Ru/TiO$_2$ and Ru/TiO$_2$/C for 5-h reaction in water phase at 180 °C.

Catalyst	Pre-treatment	Catalyst mass (mg)	TiO$_2$ mass (mg)	Conversion (%)	Acetic acid converted/TiO$_2$ mass (mmol/g)	Acetic acid converted/TiO$_2$ surface area (mmol/cm^2) ($\times 10^6$)
5%Ru/C	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	180.0	0.0	1.3	–	
TiO$_2$/C	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	205.0	61.5	15.9	250	141
Ru/TiO$_2$/C	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	398.0	119.4	54.2	440	248
Ru/TiO$_2$ P25	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	196.0	186.2	32.9	170	253
TiO$_2$ P25	None	200.0	200.0	1.5	8	12
TiO$_2$ P25	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	198.0	198.0	10.2	60	89
Ru/TiO$_2$/C (air 400)	None	200.0	60.0	1.2	20	11
Ru/TiO$_2$/C (air 400)	Pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction	200.0	60.0	18.2	303	171

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interaction between Ru and TiO$_2$ resulting in higher reducibility of TiO$_2$ and creation of more Ti^{3+} sites, as active sites for ketonization. If the moles of acetic acid converted are normalized to the mass of TiO$_2$ in the catalyst, the Ru/TiO$_2$/activated carbon displays the highest activity, as illustrated in Table 1. The high-surface area carbon support is able to stabilize TiO$_2$ in small particles, developing a high dispersion of TiO$_2$ species on the support and, at the same time, improving the tolerance of the catalyst to liquid water. This study revealed the importance of a pre-reduction of the oxide catalyst. It was found that conversion of acetic acid increased with pre-reduction of catalysts while maintaining 100% selectivity to acetone. This is interesting because one might have expected that when the catalyst is exposed to hot liquid aqueous phase during reaction, water might re-oxidize the reduced TiO$_2$ and counteract

any effect of pre-reduction treatment. However, this was not the case. As shown in Table 1, only 1.5% of acetic acid was converted to acetone over non-reduced TiO$_2$, indicating that non-reduced TiO$_2$ is inactive for ketonization. However, with a pre-reduction in H$_2$ at 250 °C, the ketonization activity of TiO$_2$ increased significantly. The effect of pre-reduction was even more pronounced when Ru was present on the catalyst due to its enhancement to the reducibility of TiO$_2$ since by itself Ru showed no activity for ketonization. This result indicates that the pre-reduction step generates reduced Ti^{3+} required for ketonization reaction.

The activated carbon support was found to prolong the life of the catalyst in aqueous phase. As shown in Fig. 2, the catalytic ketonization activity of Ru/TiO$_2$/C in water phase was kept for longer time than that of Ru/TiO$_2$. While in the 2–4 h reaction period in a batch reactor the conversion over the Ru/TiO$_2$/C catalyst increased by more than 50%, during the same period the conversion over Ru/TiO$_2$ remained unchanged, indicating that the catalyst was no longer active. That is, the presence of activated carbon seems to improve the tolerance of the catalyst to water, slowing down its deactivation. The special role played by the carbon support in water was further evidenced when n-hexane was used as a solvent. In the absence of water, the Ru/TiO$_2$ catalyst did not deactivate as fast, and the behavior of the carbon-supported catalyst was not much different from that of the Ru/TiO$_2$ catalyst. For instance, during the same period of reaction time, 2–4 h, the conversion increased by about 50% on both catalysts. These results indicate that the hydrophobic porous structure of the activated carbon may becomes saturated with organic species and impede wetting of the surface, thus preventing the irreversible catalyst deactivation by water.

Fig. 2. Catalytic activity of Ru/TiO$_2$ P25 and Ru/TiO$_2$/C catalysts for the reactions at 180 °C as a function of reaction time in water phase (a) and n-hexane (b). All the catalysts were pre-reduced in 400 psi H$_2$ at 250 °C for 3 h before reaction. Reproduced with permission from Ref. [56].

2.2. Hydrogenation of aldehydes and ketones

Another potential way of incorporating the small aldehydes and ketones into liquid fuel is to partially hydrogenate them to alcohols, which can be used as alkylating agents of phenolic compounds. A recent study [41] describes the combination of the selective hydrogenation of aldehydes/ketones and alkylation of phenolics with the resulting alcohols in a single reactor with two sequential catalyst beds. The challenge in the first catalyst bed was to hydrogenate completely the short oxygenates (aldehydes and ketones) while avoiding saturating the aromatic rings of the phenolic compounds. To find a catalyst that is able to do this selective hydrogenation, two model compounds, propanal and acetone, were converted in the vapor phase in the presence of m-cresol over a series of different metal catalysts. The series included silica-supported Cu, Ru,
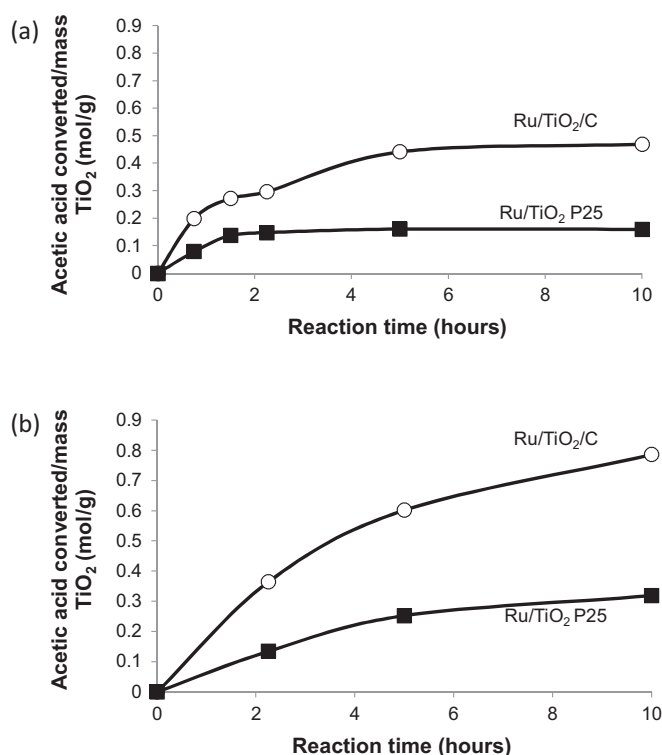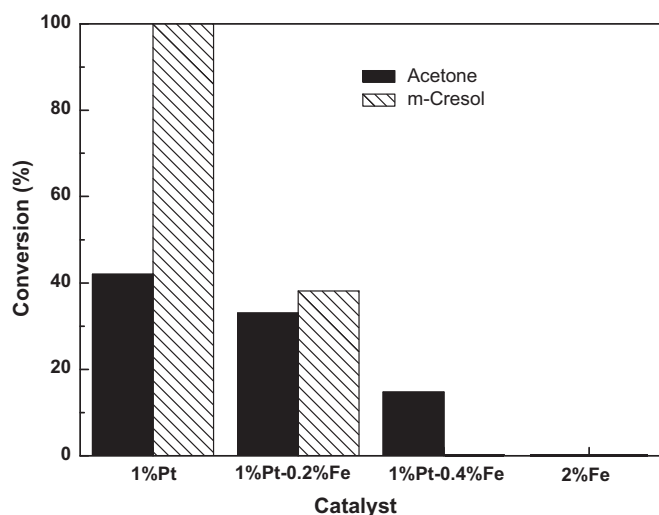
Fig. 3. Hydrogenation activity of metal/SiO$_2$ as a function of iron loading. Reaction condition: acetone:m-cresol = 4:1 (mole). TOS = 15 min. Carrier gas H$_2$ 60 ml/min. W/F = 0.5 h. 200 °C.
Reproduced with permission from Ref. [41].

Ni, Pt, and Pt—Fe. With propanal as a feed, Cu/SiO$_2$ was found to be selective toward hydrogenation of aldehyde without converting m-cresol. Hydrogenation of acetone to isopropanol turned out to be a more difficult task. In this case, the 5%Cu/SiO$_2$ catalyst that was effective for hydrogenating propanal was inactive for acetone. On the other hand, Pt/SiO$_2$ was able to hydrogenate acetone but was also very active toward aromatic ring hydrogenation. However, the bimetallic Pt—Fe/SiO$_2$ catalyst exhibited a remarkable increase in selectivity toward hydrogenation of carbonyl group, while leaving the aromatic ring unaffected. Different Fe/Pt ratios were compared in Fig. 3. While the addition of Fe inhibits both the hydrogenation of the ketone and the phenolic, the drop in the latter was much more pronounced than that of the acetone. For instance, the 1%Pt–0.4%Fe/SiO$_2$ catalyst showed zero conversion of m-cresol but kept a significant activity for acetone hydrogenation. The pure Fe catalyst was inactive. Moreover, as space time W/F (catalyst weight/feed flow rate) increases, the yield of acetone hydrogenation products increased without saturating the aromatic ring. After completely converting acetone to isopropanol, this alcohol was used to alkylate m-cresol over an acidic zeolite H-Beta, yielding alkylated products. The use of hydrophobic zeolites to conduct alkylation in aqueous phase is discussed below (see Section 4.1).

Another example of combining selective hydrogenation with C—C coupling was the catalytic conversion of lactic acid (2-hydroxypropanoic acid) in aqueous phase over Pt/Nb$_2$O$_5$ [57]. Sugar-derived lactic acid was first hydrodeoxygenated to produce two intermediates: acetaldehyde and propanoic acid. The formation of acetaldehyde involved C—C bond cleavage by means of decarbonylation/decarboxylation catalyzed by Pt and acid sites. The formation of propanoic acid was proposed to occur by removal of an OH group via C—O cleavage. Once formed, acetaldehyde undergoes self-aldol condensation to form butanal, whereas propanoic acid was converted to 3-pentanone via ketonization. The bifunctional catalysts Pt/Nb$_2$O$_5$ allowed this series of reactions to be carried out in a single reactor, in which hydrogenation can be achieved on Pt sites and dehydration, decarboxylation, and condensation reactions can be catalyzed by acidic Nb$_2$O$_5$. Concentrated aqueous solution of lactic acid (60%) was efficiently converted over 0.1%Pt/Nb$_2$O$_5$ to produce about 24% of coupling products. The combination of deoxygenation followed by condensation reactions is

a general protocol that could be also applied to other small oxygenates compounds.

3. Conversion of sugar-derived compounds

Acid-catalyzed dehydration of sugars including xylose, fructose, and glucose results in the formation of two main compounds: furfural and 5-hydroxymethyl furfural (HMF). Both compounds are very reactive. So it is vital to convert them into more stable and less reactive compounds before they undergo undesired reaction, i.e., humins polymerization. As proposed above, the best option is to utilize their functionalities to make C—C coupling reaction to increase molecular weight compounds before deoxygenation. Two alternatives can be considered: (i) aldol condensation and subsequent hydrogenation, or (ii) oxidation to the corresponding acids, followed by ketonization/hydrogenation/deoxygenation.

3.1. Aldol condensation of furfurals and ketones/aldehydes followed by hydrogenation

Aldol condensation combined with hydrogenation is an important process to produce large hydrocarbon molecules. It is generally catalyzed by a base and allows the formation of C—C bond between carbonyl containing compounds via the so-called "enolate mechanism". The basic catalyst abstracts an H atom from an α-C (adjacent to a CO group) to form an intermediate carbanion (enolate ion) species, which then attacks the C atom of the CO group of another molecule to form a C—C bond. Although HMF and furfural do not possess any α-H atom, it is possible to perform cross condensation with small ketones and aldehydes, which contain α-H atoms. This reaction has been studied extensively in literature in both single and biphasic liquid systems. Numerous solid base catalysts have been proved to be active for this reaction, including oxides of alkaline earth metals [58–60], amine-functionalized MCM-41 [61] and hydrotalcites [62]. Homogeneous catalysts, such as NaOH, have been also used in biomass conversion studies [63].

Huber et al. [64] investigated aldol condensation of HMF and furfurals with acetone/propanal in water–methanol solvent over MgO–ZrO$_2$, NaY, and nitrogen-substituted NaY (Nit-NaY). They observed a primary condensation monomer formed from the reaction of furfural with acetone and a dimer formed from the secondary reaction of the monomer with another furfural. Their results of furfural/propanal, HMF/acetone, and HMF/propanal condensation reactions over the tested catalysts are reproduced in Table 2. While the MgO–ZrO$_2$ catalyst exhibited the highest aldol condensation activity, reaching 51.4% conversion of HMF, NaY had the lowest conversion (14.1%). The Nit-NaY sample also showed a high activity but with much higher selectivity to monomers than MgO–ZrO$_2$. The higher activity of Nit-NaY over unpromoted-NaY indicates that the incorporation of N into the framework may increase the basic strength of the zeolite. Also, the higher selectivity toward monomers exhibited by the zeolites was attributed to shape selectivity effects due to the small cage size of the zeolite structure, which prevents the secondary condensation reaction that leads to dimers. The stability of the catalysts was tested by conducting recycle runs. It was found that the MgO–ZrO$_2$ catalyst retained most of the activity but Nit-NaY was unstable and lost approximately 70% of its initial activity. Interesting questions about the stability of these catalysts remain unanswered.

In an earlier study, cross-condensation of various ketones and aldehydes including furfural with acetone was investigated on diamino-functionalized mesoporous basic catalysts in liquid phase [61]. The catalysts prepared by anchoring 3-trimethoxysilylpropylethylenediamine on calcined MCM-41 showed good activity and recyclability toward aldol condensation

Table 2
Summary of aldol condensation reaction results of fufural/HMF with acetone/propanal over MgO–ZrO$_2$, NaY and Nit-NaY at 120 °C in water/methanol (1:1) solvent.

Reaction	Reactant (1:1 by molar)	Catalyst	Reaction time (h)	Disappearance of furfurals (%)	Selectivity to aldol products (%)	Distribution (%)	
						Monomer	Dimer
1	HMF/acetone	MgO–ZrO$_2$	16	51.4	91.9	56.5	43.5
2	HMF/acetone	NaY	16	14.1	89.7	85.9	14.1
3	HMF/acetone	Nit-NaY	16	40.1	80.9	72.7	27.3
4	Furfural/propanal	MgO–ZrO$_2$	16	60.4	90.0	100.0	–
5	Furfural/propanal	NaY	16	6.7	38.6	100.0	–
6	Furfural/propanal	Nit-NaY	16	55.5	104.7	100.0	–
7	HMF/propanal	MgO–ZrO$_2$	16	86.8	57.0	100.0	–
8	HMF/propanal	NaY	16	26.4	39.6	100.0	–
9	HMF/propanal	Nit-NaY	16	86.4	53.7	100.0	–

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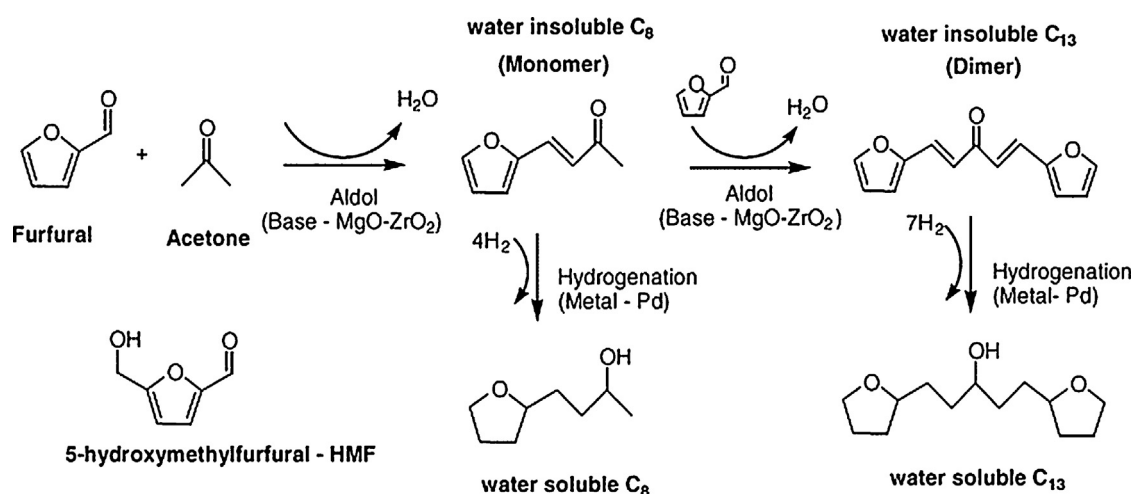
Fig. 4. Reaction pathway for aldol-condensation of furfural (or HMF) and acetone, followed by hydrogenation of aldol-condensation products. Reproduced with permission from Ref. [59].

at low temperatures (50 °C). Conversions ranging from 70 to 100% were obtained with 0.2 g catalysts for 70 mmoles of ketone feed, but the investigation was limited to organic solvents.

Dumesic et al. [59,60] developed a bifunctional Pd/MgO–ZrO$_2$ catalyst to perform aldol condensation of furfural and HMF with acetone in aqueous phase. The condensation reaction was followed by sequential hydrogenation to produce C8–C9 (monomer) or C13–C15 (dimer) products, as illustrated in Fig. 4. The reaction was carried out under mild conditions (50–120 °C, 10 bar) in inert gas. The interesting concept of reactive separation was adopted in this study. As the aldol-condensation occurred in aqueous phase, the monomer and dimer products precipitated out of aqueous phase due to their low solubility in water. When the condensation was complete, the aqueous layer was evaporated off, and an organic solvent (hexadecane) was incorporated. H$_2$ was introduced to this organic medium until a pressure of 55 bar was reached to conduct the hydrogenation step at 120 °C. This process was found to reach yields of more than 80% of the original carbon. Also, it was shown that the catalyst could maintain most of its activity and selectivity for three runs without regeneration and can be regenerated completely through an intermediate calcination at 600 °C. As demonstrated in Fig. 5, for recycle runs #2 and #3, without any intermediate regeneration, the selectivity to the dimer only decreased by about 18% while the carbon yield remained high (>90%). Upon a calcination pretreatment, the selectivity and activity of catalysts recovered to their original level (run #4).

The use of bifunctional catalysts and biphasic systems is a very promising approach but the need to change solvents between two reaction steps is seen as a hurdle toward practical applications. This problem was tackled in a subsequent study [63] by simultaneously using THF in the organic phase and adding NaCl to the aqueous phase to further reduce the solubility of the condensation products. In this biphasic system, the condensation products transferred, as soon as they were formed, from the NaCl-containing aqueous phase to the THF phase. Hydrogenation takes place in this phase allowing for a continuous reaction operation. However, large amounts
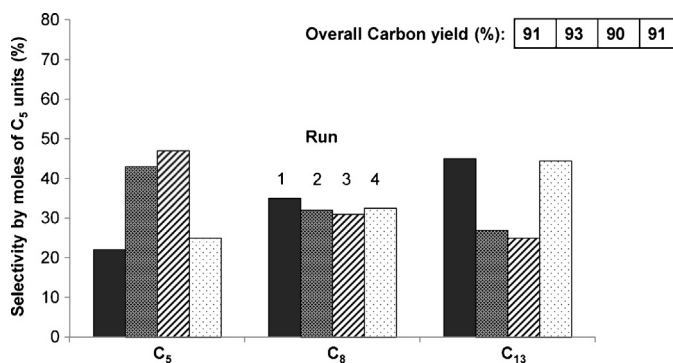
Fig. 5. Selectivity based on C5 (furfural) units and overall carbon yields in the aqueous phase after aldol condensation–hydrogenation over fresh and recycled 5% Pd/MgO–ZrO$_2$ catalyst. Bar 1 (black): fresh catalyst; bar 2 (dark gray): first recycle without calcination; bar 3 (light gray): second recycle without calcination; bar 4 (white): third recycle with calcination. More detailed in reaction conditions can be found in Ref. [59].

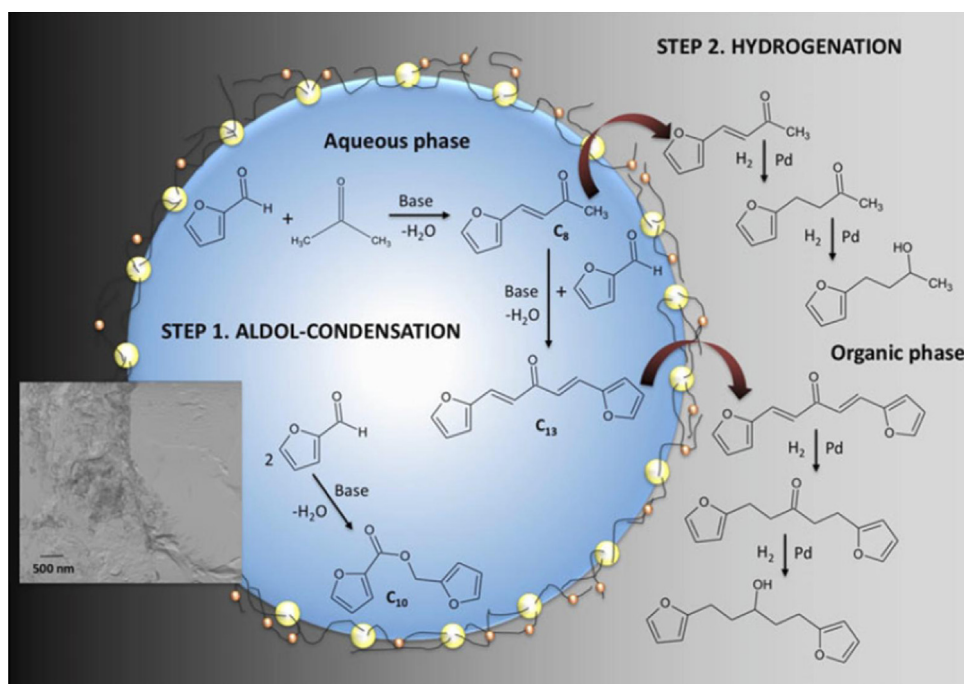Reproduced with permission from Ref. [59].

Fig. 6. Schematic illustration of the aldol condensation and sequential hydrogenation at the water/oil interface in nanohybrid-stablizied emulsions. Reproduced with permission from Ref. [40].

of homogeneous base (NaOH) were needed to catalyze the aldol condensation reaction.

In another example of simultaneous conversion in a biphasic system, Zapata et al. [40] used an amphiphilic nanohybrids catalysts which can effectively stabilize water/oil emulsions and conduct simultaneously condensation/hydrogenation of acetone and furfural. Fig. 6 describes this concept. As the aldol condensation proceeds, the coupling products migrate to the organic phase where they can be selectively hydrogenated. The advantages of this approach include easy separation of products allowing continuity of reaction and increased reaction rate due to high interfacial areas. Nanohybrids prepared with carbon nanotubes fused to various basic oxides (MgO, MgO/Al$_2$O$_3$, TiO$_2$, ZnO, Ce$_x$Zr$_{1-x}$O$_2$, and V$_2$O$_5$) were tested as aldol condensation catalysts in the emulsion system. Major products observed from cross condensation were monomer C$_8$ (C$_3$ + C$_5$) and dimer C$_{13}$ (C$_5$ + C$_3$ + C$_5$); small amounts of Canizzaro products, i.e., furfuryl alcohol, furoic acid and their esters were also observed. It was found that the carbon nanotube/MgO nanohybrids displayed the highest activity. It is worth noting that due to the presence of carbon nanotubes over oxides, the nanohybrids showed much higher tolerance to water leaching than bare oxides. Also, it was found that the aldol condensation conversion in the biphasic emulsion was significantly higher than the reaction in single aqueous phase. Fig. 7 shows the conversion of furfural and acetone in a batch reactor as function of reaction time. As it can be seen, the catalyst did not deactivate during this reaction period, as indicated by the linear increase in conversion as a function of time.

After completing the aldol condensation step, hydrogenation of the condensation products was carried out in organic phase using Pd supported on hydrophobic support, i.e., purified single walled carbon nanotube. The hydrophobicity of nanotubes prevented Pd from entering aqueous phase. As a result, the slow mass transfer of water-soluble compounds (e.g. unconverted acetone) prevents any hydrogenation in organic phase. Table 3 summarizes the product distribution of combined aldol condensation/hydrogenation reactions in biphasic system. These results highlight the application of the emulsion biphasic system for bio-oil upgrading. The advantage

of conducting sequential reactions in a single reactor instead of two is significant and it could be also applied to other liquid phase reactions.

3.2. Oxidation of sugars to acids

Another strategy to incorporate sugar-derived compounds into the fuel range is to use a selective oxidation step to carboxylic acids, which as discussed above, can be enlarged via ketonization and subsequently deoxygenated. It has been suggested that liquid phase oxidation can proceed on metal surfaces via a dehydrogenation step followed by oxidation by dissociatively adsorbed oxygen, also known as oxidative dehydrogenation mechanism [65–69]. The conversion of sugars to organic acids on metal catalysts has been studied extensively for a long time [65–67]. As recently reviewed [68,69], the selective oxidation of sugars to monoacids
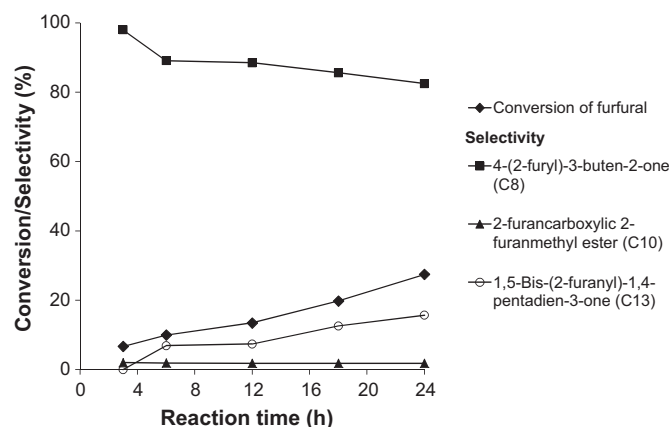

Fig. 7. Product yield and overall conversion of furfural of aldol condensation of furfural:acetone (1:5) over multi-walled carbon nanotubes/MgO nanohybrids at 100 °C as function of reaction time.
Reproduced with permission from Ref. [40].

Table 3
Final product distribution of the aldol condensation/hydrogenation of furfural and acetone in a biphasic emulsion system using a physical mixture of SWCNT/MgO and Pd/Purified SWCNT. Reaction conditions: 10 h at 80 °C in 300 psi He for aldol condensation and 17 h at 100 °C in 300 psi H2 for hydrogenation reaction.

mmole compound	Feed				Aldolcondensation				Hydrogenation			
	Aqueous	Organic	Heavy	Total	Aqueous	Organic	Heavy	Total	Aqueous	Organic	Heavy	Total
(structure)	12.2	2.3	6.0	20.5	8.0	0.6	1.6	10.2	3.3	0.2	0.7	4.2
(structure)	13.7	6.1	80.4	100.2	34.8	7.1	31.7	73.6	15.1	3.9	27.0	46.0
(structure)	–	–	–	–	0.9	–	0.2	1.1	2.4	0.6	2.5	5.5
(structure)	–	–	–	–	1.0	1.1	5.4	7.5	–	0.8	3.7	4.5
(structure)	–	–	–	–	–	–	–	–	–	2.5	0.4	2.9
(structure)	–	–	–	–	–	–	–	–	0.4	–	0.1	0.5
(structure)	–	–	–	–	1.3	–	0.1	1.5	2.5	–	0.5	3.0
(structure)	–	–	–	–	0.9	–	0.2	1.1	1.1	0.0	0.0	1.1
(structure)	–	–	–	–	–	–	–	–	2.0	–	2.0	2.2
(structure)	–	–	–	–	–	2.8	0.2	3.0	0.0	2.2	0.0	2.2
(structure)	–	–	–	–	–	–	–	–	–	3.1	0.3	3.4
(structure)	–	–	–	–	–	–	–	–	0.2	–	0.2	0.4
Carbon balance	100.0%				92.8%				83.4%			

Reproduced with permission from Ref. [40].

(e.g. gluconic acid) can be achieved over Pt- or Pd-based catalysts. It has been shown that the addition of bismuth (Bi) as a promoter to Pt or Pd greatly enhances activity and selectivity to mono-acid compounds [65,66,70–72]. For example, the rate of glucose oxidation increased more than 20 times upon addition of Bi to Pd/C [66]. Different explanations for the promoter effects of Bi on oxidation rate have been suggested. Mallat et al. [65] proposed that the presence of Bi decreases the size of Pt active site ensembles thus suppressing the poison formation, i.e., aldol-dimerization of carbonyl compounds. Wenkin et al. [72] postulated that the formation of Bi–glucose or Bi–gluconate complexes facilitates glucose dehydrogenation and, therefore, increases the overall rate of oxidative process. The complexation allows either a better orientation of the substrate molecule toward the noble metal surface, or the formation of a Bi–O bond making glucose deprotonation and subsequent hydride abstraction easier. It also has been found that catalyst structure such as metal particle size or catalyst support and reaction conditions including pH and oxygen pressure have dramatic influences on catalyst deactivation and reaction rates [69,73]. These are important aspects that have not yet been studied in a mixture with the complexity of bio-oil. Therefore, this area may open a number of interesting opportunities for catalysts development and optimization of selectivity and performance.

The direct transformation of fructose into 2,5-furandicarboxylic acid (FDCA) via consecutive dehydration and oxidation was studied by Kroger et al. [74]. Two systems were designed to test this concept, one by phase separation with a membrane, the other by encapsulating the oxidation catalyst in silicone beads (see Fig. 8). By using Pt–Bi/C as the oxidation catalyst, an FDCA yield of 25% from fructose was achieved. The overall reaction rate was controlled by diffusion of HMF to the oxidation catalyst. The major drawback was a high degree of levulinic acid formation as the by-product. Higher yields have been obtained in aqueous medium when 5-hydroxymethyl-2-furfural (HMF) was used as a feed instead of fructose [75]. This reaction was found to proceed via initial oxidation of the aldehyde to form an intermediary 5-hydroxymethyl-2-furancarboxylic followed by oxidation of the hydroxymethyl group to produce dicarboxylic acid, with 2,5-furandicarboxylic acid (FDCA) as the major product.

Pasini et al. [76] have shown that TiO$_2$-supported Au is a highly active catalyst for the oxidation of HMF to FDCA; 71% yield was obtained at 30 °C after 18 h under 20 bar of O$_2$ in basic aqueous phase. Lower pressures of O$_2$ lead to the formation of more intermediate byproducts and consequentially lower FDCA yields. They have also shown that addition of Cu to Au enhances oxidation activity. For example, when 0.36% Cu was added to a 1.14% Au/TiO$_2$ (anatase) a 100% increase in activity was observed over the monometallic Au catalyst [76]. Yields above 90% with 100% selectivity to dicarboxylic product were achieved at 95 °C in basic medium under lower pressure (10 bar) of O$_2$. The enhanced performance of the
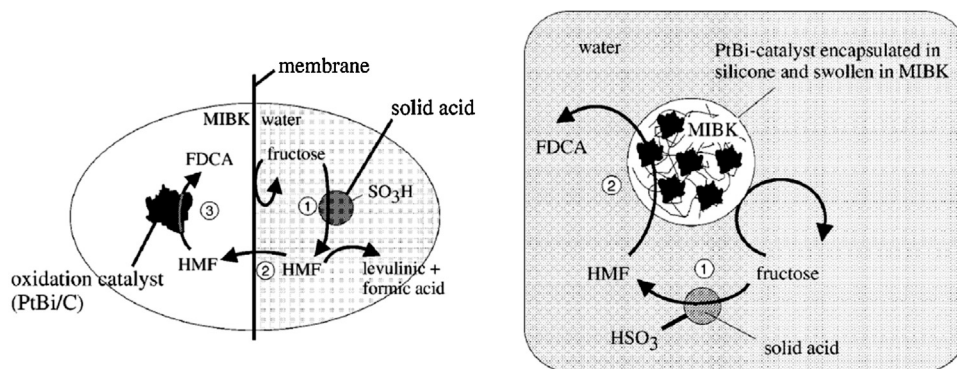
Fig. 8. Schematic illustration of integrated fructose dehydration/HMF oxidation in membrane reactor (left), and in batch reactor (right). Reproduced with permission from Ref. [74].

bimetallic catalysts has been ascribed to Au site isolation caused by alloying.

Similarly, Corma et al. [77] have found that in aqueous phase under mild conditions (65–130 °C, 10 bar in air) Au/CeO_2 was even more active and selective to FDCA than Au/TiO_2. Increased reaction temperature had a positive effect on conversion, but it caused the formation of degradation products, i.e., ring opening, furoic acid, and furane. An important aspect to point out is that, in most cases, addition of a homogeneous base was needed to help desorbing the acid product from the catalyst surface. By contrast, Ebitani et al. [78] have recently reported that hydrotalcite-supported Au exhibited high FDCA yields in base-free aqueous phase at 95 °C under atmospheric O_2 flow.

4. Conversion of lignin derived compounds

The lignin-derived compounds in bio-oil comprise phenolic compounds ranging from single-ring aromatic oxygenates such as cresol to multi-ring aromatics. The single-ring compounds could be effectively alkylated with short alcohols followed by mild hydrodeoxygenation to form C10–C13 aromatics. In this section, we review how these two steps can be accomplished in liquid phase under mild conditions.

4.1. Alkylation of phenolics with alcohols

Zeolite-based catalysts have been extensively investigated for alkylation of aromatic compounds for many years [79,80]. Alkylation of aromatics with short alcohols and olefins has been widely employed in industry [81], both in vapor and organic liquid phases. However, application of zeolites for alkylation in aqueous phase remains a big challenge since most zeolites lose crystalline structure and catalytic activity when exposed to water [82,83]. Incorporation of Sn into Beta zeolites framework were shown to create more Lewis acid sites, which helped to provide adequate number of active sites to retain high catalytic activity for several acid-catalyzed reactions in the presence of water. [84,85]. However, loss of activity by addition of water was still observed.

Recently, Zapata et al. [86] reported that sylilation of the external surface of zeolites produces hydrophobic zeolites with improved tolerance to hot liquid water. They used hydrophobic functionalized HY zeolites to catalyze the alkylation of m-cresol with isopropanol in aqueous phase at 200 °C. An HY zeolite (Si/Al = 30) was functionalized with long-alkyl-chain octadecyltrichlorosilane (OTS). An important characteristic of these zeolites is that while the external surface is functionalized to be hydrophobic, the internal Bronsted sites remained unaltered, which preserved the catalytic activity of the zeolite. FTIR of adsorbed

pyridine demonstrated that the density of the Bronsted sites was practically unchanged after functionalization.

Table 4 compares catalyst activity in single aqueous medium and emulsion at 200 °C of hydrophobic functionalized and untreated zeolites. It was shown that hydrophobic OTS-functionalized zeolite exhibited a much higher stability of alkylation activity than the untreated zeolites. For example, during the first 3 h reaction in the biphasic system in a batch reactor, the conversion of m-cresol with the untreated zeolite was 9% and 20% with the functionalized zeolite. More importantly, during the following 2 h, the latter increased to 37% while the former stayed at 9% (see Fig. 9). In a second run that reused the same catalysts, while the untreated zeolite had become inactive, the functionalized zeolite retained more than 85% of its original activity. Characterization of the spent catalysts with TEM, SEM, BET, and XRD clearly showed that hydrophobization of the external surface prevents the collapse of the crystalline structure. After a few hours under reaction in the biphasic system at 200 °C,

(1) The untreated HY zeolite lost 50% of the XRD intensity, 70% of its BET surface area, and became mesoporous (i.e. the meso/micro pore ratio increased by 150 times).
(2) The OTS functionalized zeolite only lost less than 10% of its XRD intensity, 15% of its BET area, and the meso/micro pore ratio increased only by a factor of 3.
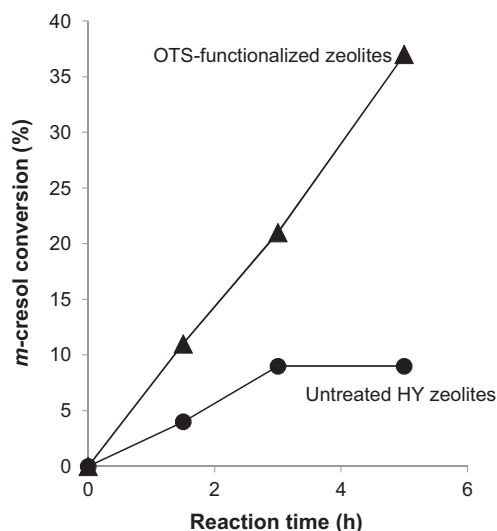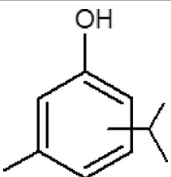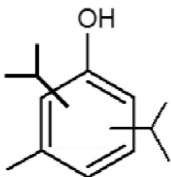

Fig. 9. Comparison in m-cresol conversion for alkylation reaction over bare and octadecyltrichlorosilane (OTS)-functionalized zeolites at 200 °C and 700 psi He. Reproduced with permission from Ref. [86].

Table 4
Comparison in activity for alkylation in single phase vs. emulsion phase using untreated and octadecyltrichlorosilane (OTS) functionalized HY zeolites (Si/Al = 30). The feed had a total concentration of 2 M with 2-propanol:m-cresol molar ratio of 3:1.

	Single aqueous phase				Emulsion (water/decalin)			
	Untreated HY		OTS-functionalized HY		Untreated HY		OTS-functionalized HY	
	1.33 h	3 h	1.33 h	3 h	1.33 h	3 h	1.33 h	3 h
(structure)	1.8	2.3	2.22	7.3	2.6	6.6	6.9	13.0
(structure)	0.2	1.1	0.6	3.0	1.0	2.5	3.0	6.5
m-Cresol conversion (%)	2.0	3.3	2.8	10.3	3.6	9.1	9.9	19.5

Reproduced with permission from Ref. [86].

The SEM and TEM images showed almost no change in topology for the functionalized zeolite, but a dramatic change for the unfunctionalized zeolite, which composed of amorphous domains that are a product of nucleation and re-precipitation steps that occur in liquid water. These phenomena do not occur when direct contact of zeolite external surface with liquid water is prevented. Fig. 10 illustrates the dramatic changes observed in the topology of the regular HY zeolite after 22 h in biphasic system (200 °C), in comparison to the unnoticeable changes observed with the hydrophobized zeolite.

4.2. Hydrodeoxygenation of phenolic compounds

Phenolics are lignin-derived compounds that include a variety of oxygenated functionalities, such as hydroxyl, methoxy, carbonyl, and aldehyde groups. These compounds include phenol, catechol, anisole, guaiacol, vanillin, syringol, eugenol, and their alkylated derivatives. In general, these compounds are prone to oligomerization and result in heavier compounds during condensation of pyrolysis vapors while kept in storage, and when re-heated for upgrading process. For this reason, it is important to selectively convert the unstable oxygen functional groups, if possible, in liquid phase at moderate temperatures under medium to high pressure of H_2 in the presence of metal catalysts. Under these conditions,

re-vaporization of condensed bio-oil is avoided and hydrogen utilization is limited to the removal of the most undesirable active functionalities. Lercher et al. [87–89] have recently studied a new route for conversion of lignin-derived phenolics in aqueous phase using metal catalysts (Pd or Ni) in the presence of acids (H_3PO_4 or Nafion/SiO$_2$). From the evolution of products as a function of reaction time in a batch reactor (see Fig. 11), these authors have identified the main reaction pathways and revealed the influence of some reaction parameters on the overall reaction scheme, including reaction temperature and Bronsted acid site concentration. The model feeds studied consist of phenol, catechol, anisole, and guaiacol. The proposed reaction pathways and product distributions as a function of time are displayed in Fig. 12.

The conversion pathways for the different oxygen functionalities are summarized as follows:

(a) *Hydroxyl group*: Under the conditions investigated, phenol is first converted to cyclohexanone. This path is thought to occur via a partial hydrogenation of the aromatic ring to an unsaturated cyclic alcohol, followed by tautomeric isomerization that results in saturated ketone. Ketone is hydrogenated to cyclohexanol, followed by dehydration and hydrogenation to cyclohexane. A similar path has been suggested by Jones et al. [90].
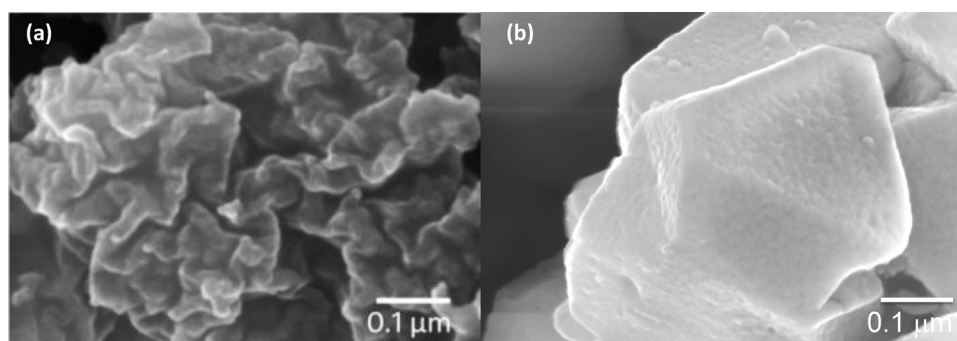

Fig. 10. Enhanced hot liquid water tolerance on silanized hydrophobic HY zeolite. SEM images of two zeolite samples exposed to liquid water at 200 °C for 22 h: (a) bare HY zeolite and (b) octadecyltrichlorosilane (OTS) functionalized HY zeolite.
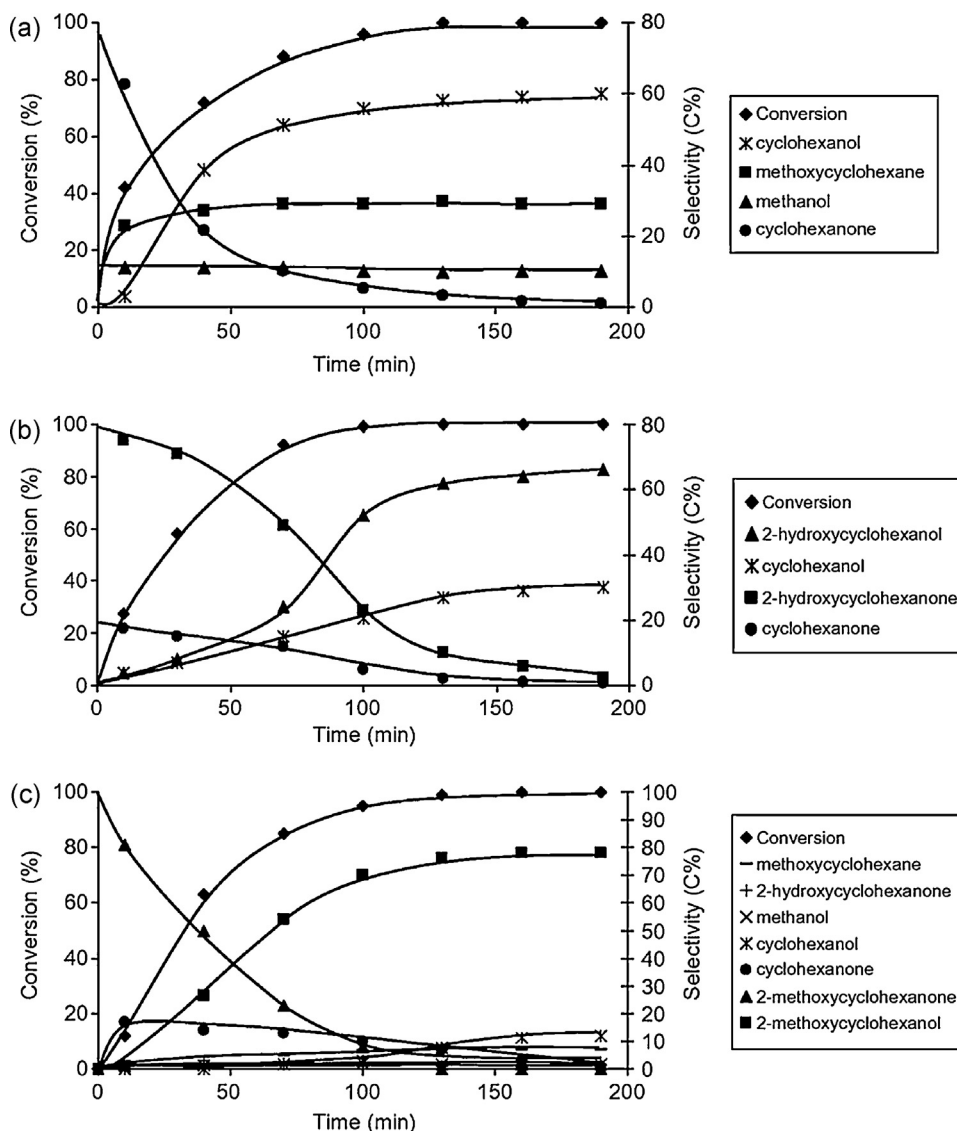
Fig. 11. Product distribution after hydrogenation of phenolic monomers: (a) anisole, (b) catechol, and (c) guaiacol. Reaction conditions: reactant (0.0106 mol), Pd/C (5 wt.%, 0.020 g), H_3PO_4-H_2O (0.5 wt.%, 80 ml), 423 K, 5 MPa H_2 (ambient temperature), stirred at 1000 rpm.
Reproduced with permission from Ref. [87].

Catechol with two adjacent hydroxyl groups in the ring is also hydrogenated and dehydrated to produce cyclohexanol by going through phenol or cyclohexenone as the intermediates. Lercher et al. [88] have concluded that for all phenolics the metal function is required to start the reaction by a partial hydrogenation step, while the acid function is required for hydrolysis and dehydration.

(b) *Methoxy group*: In aqueous phase, the main reaction pathway for compounds containing a methoxy group is hydrolysis that produces methanol and leaves a hydroxyl group on the ring. For example, anisole produces methanol and phenol, which can be subsequently deoxygenated by a sequence of hydrogenation/dehydration steps described above. Alternatively, the removal of the methoxy group via transalkylation has been found to occur in vapor phase, without the participation of water [91]. Transalkylation of anisole produces cresol and phenol [92]; guaiacol produces catechol and methylanisole, which undergo subsequent transalkylations producing cresol and xylenols.

(c) *Carbonyl group*: Another interesting pathway identified by Jones et al. [90] for the conversion of phenolics resulted in the formation of bicyclic compounds. These authors observed the formation of 2-cyclohexyl cyclohexanone during phenol hydrodeoxygenation over metal-containing zeolites. Since the appearance of this bicyclic compound correlated with the appearance of cyclohexanone (see (a) above), they ascribed its formation to the aldol condensation of cyclohexanone over the acid sites of the zeolite.

It has been recently pointed out that additional benefits can be gained when hydrodeoxygenation is carred out in biphasic system (e.g. water and a hydrophobic liquid). Valuable products can be separated into the other phase, preventing undesired secondary reactions (e.g. thermal decomposition), or the need for separation steps such as distillation that might damage heat-sensitive compounds. Moreover, when an emulsion is generated the interfacial surface area is greatly increased, thus enhancing the rate of mass transfer and improving selectivity to products of interest. When surfactants are used to enhance molecule transfer between phases,
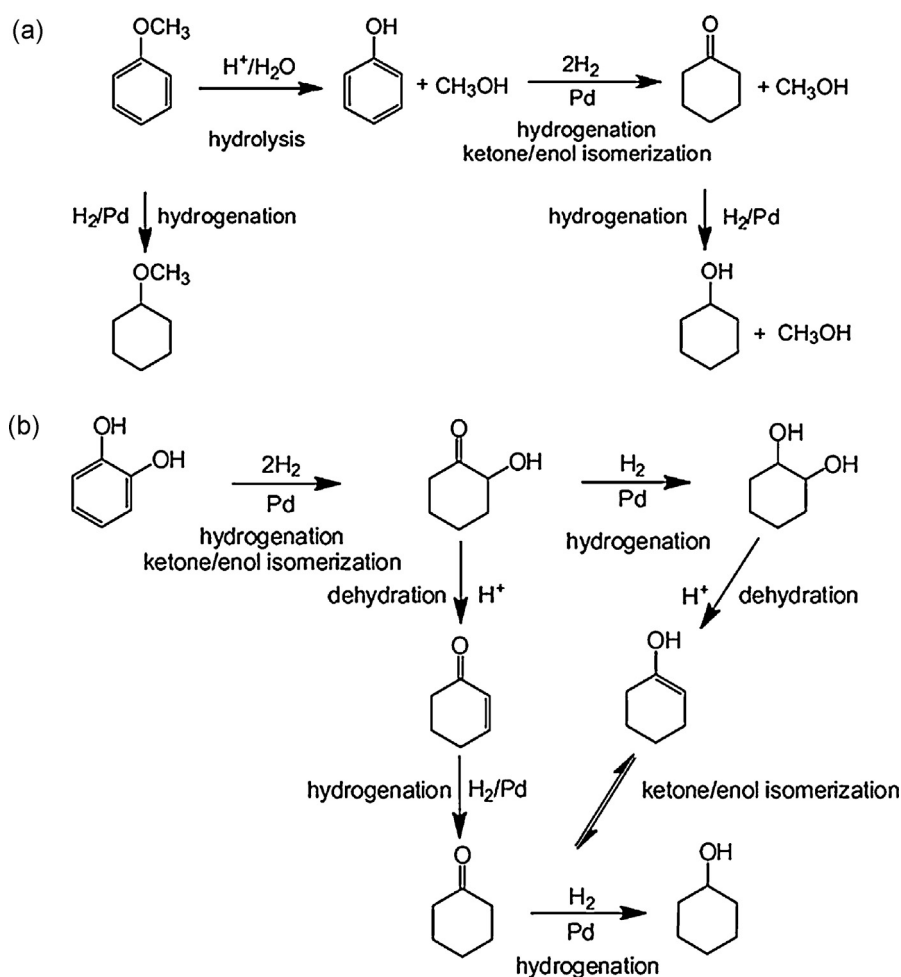
Fig. 12. Proposed reaction pathway for aqueous-phase conversion of model phenolics: (a) anisole and (b) catechol to cyclohexanol with Pd/C catalyst and H_3PO_4 component. Reproduced with permission from Ref. [87].

a major drawback is the impossibility of breaking the emulsion after reaction, or separating the surfactant. Crossley et al. [93] developed a biphasic hydrotreating process for upgrading bio-oils in which surfactants are replaced by amphiphilic catalyst particles that can be readily recovered and reused after each catalytic cycle. This novel methodology combines the advantages of phase transfer and heterogeneous catalysis. To illustrate the application, Pd supported on carbon nanotube/metal oxide hybrid was used as amphiphilic catalyst that is located at the interface between two phases. The product distribution for the conversion of vanillin in the two-phase system is summarized in Fig. 13, which demonstrates the concept of simultaneous reaction and product separation.

Table 5
Effective hydrogen-to-carbon ratio H/C_{eff} of natural gas and typical biomass compounds.

|	Compounds	Chemical formula	C	H	O	$(H/C)eff$
Natural gas	Methane	CH_4	1	4	0	4.00
	Ethane	C_2H_6	2	6	0	3.00
	Propane	C_3H_8	3	8	0	2.67
	Butane	C_4H_{10}	4	10	0	2.50
Crude oil	Benzene	C_6H_6	6	6	0	1.00
	Toluene	C_7H_8	7	8	0	1.14
	Paraffins	C_nH_{2n+2}	n	$2n+2$	0	>2.00
	Naphthenes	C_nH_{2n}	n	$2n$	0	2.00
Biomass derived compounds	Cellulose	$(C_6H_{10}O_5)_n$	6	10	5	0.00
	Acetic acid	$C_2H_4O_2$	2	4	2	0.00
	Acetone	C_3H_6O	3	6	1	1.33
	Acetol	$C_3H_6O_2$	3	6	2	0.67
	Levoglucosan	$C_6H_{10}O_5$	6	10	5	0.00
	Furfural	$C_5H_4O_2$	5	4	2	0.00
	Hydroxymethylfurfural	$C_6H_6O_3$	6	6	3	0.00
	Cresol	C_7H_8O	7	8	1	0.86
	Guaiacol	$C_7H_8O_2$	7	8	2	0.57
	Phenol	$C_6H_6O_3$	6	6	1	0.67
	Vanillin	$C_8H_8O_3$	8	8	3	0.25
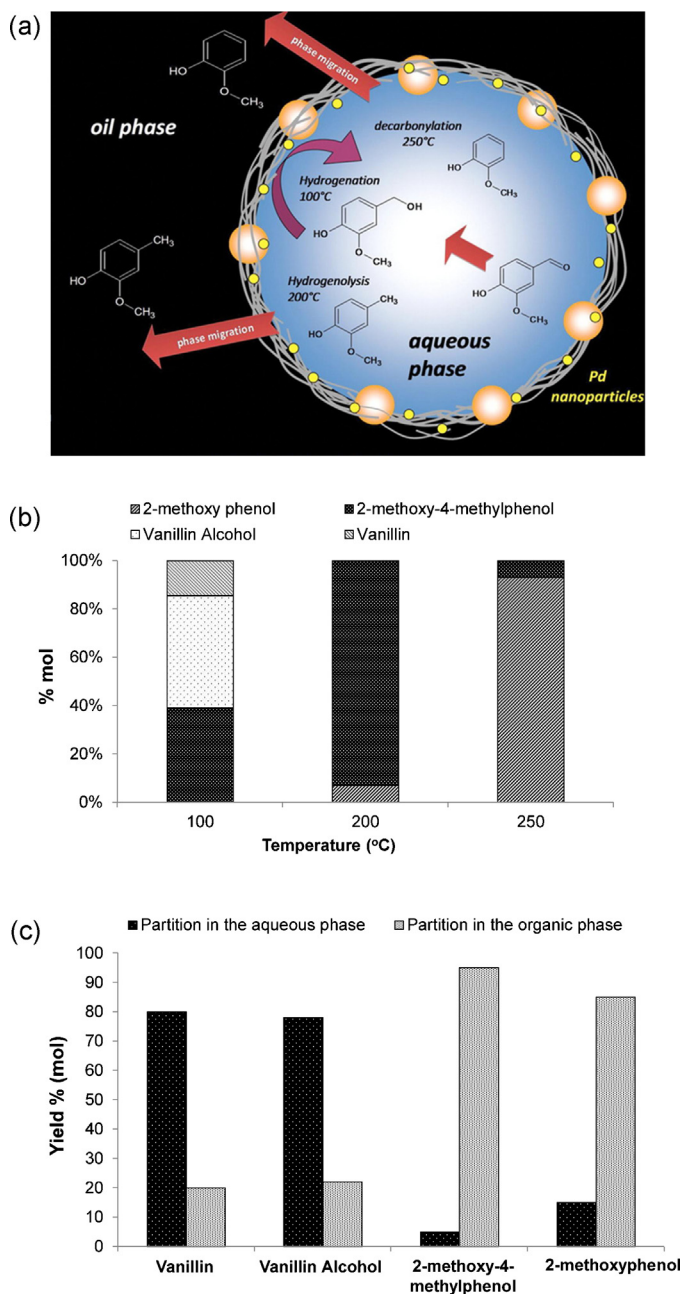
Fig. 13. (a) Schematic illustration of the reactions at the water/oil interface in the solid-stabilized emulsions. Depending on reaction condition and solubility, the products can selectively distribute in either oil or aqueous phase. (b) Total weight fraction of the various products as a function of temperature after 30-min reaction in a batch reactor, from gas chromatographic analysis of each phase (combined). (c) Partition of the various products as in (b) between the individual aqueous and organic phases.

Reproduced with permission from Ref. [93].

This study represents a major process improvement in bio-oil upgrading in which, by the use of multiphase (oil/emulsion/water) system a continuous process is made possible along with full conversion on both sides of the emulsion followed by constant product removal with high efficiency.

5. Economic aspects

The proposed upgrading approach is based on a multi-stage pyrolysis process, which, in contrast to conventional fast pyrolysis, would include thermal fractionation, as a result it might demand a higher initial investment and operating cost due to its more complex design and process control such as temperatures, heating, and residence time. However, as mentioned above, by using this multi-stage approach, the pyrolysis products will be less complex and more amenable to catalytic upgrading. This will greatly reduce the cost of handling, storage and upgrading, which comprise the highest fraction in overall biofuel production cost [94].

In addition, the liquid-phase upgrading approach following the multi-stage pyrolysis offers unique advantages over other approaches. However, it still requires a considerable amount of H_2 for hydrodeoxygenation steps. One important question is what are the most effective sources of hydrogen to be used in biomass conversion. It is clear that whenever another source of hydrogen is available, biomass should not be used as a source of hydrogen for biofuels production. First, being a finite amount of biomass, one should maximize the carbon yield from biomass rather than hydrogen as the effective H/C ratio in biomass is exceedingly low. Therefore, more fossil carbon would be replaced by using a fossil source of hydrogen than biomass. Table 5 show the effective hydrogen-to-carbon ratio H/C_{eff} of natural gas and typical biomass compounds. The effective H/C ratio, defined as $(H/C)_{eff} = (H-2O)/C$, was first introduced by Chen and Koenig [95], who studied the conversion of carbohydrates over ZSM-5 catalyst. This is an index for the required chemistry for the conversion of biomass derived compounds in catalytic cracking. The H/C_{eff} for natural gas and petroleum based feedstock ranges from 1 (for benzene) to 4 (for methane), whereas that of biomass-derived compounds is mainly 0. From the economic point of view, the difference is obvious. For example, Padro and Putsche [96,97] estimated the cost of producing hydrogen by steam reforming of pyrolysis vapors to be in the range of $8.86/GJ to $15.52/GJ depending of facility size and biomass type, which is considerably higher than the cost of commercial natural gas steaming of $3/GJ. Therefore, from both desirable outcomes, i.e., maximizing fossil carbon replacement and minimizing cost in many areas [98], natural gas should be used as a source of hydrogen for biomass conversion.

6. Conclusion and outlook

Bio-oil is a complex mixture of numerous compounds of low vapor pressure and heating value, high water solubility, and reactivity. Hence, upgrading is necessary for a more stable and energy-intensive liquid product. Catalytic upgrading in liquid phase at mild temperatures is foreseeably an economically and technically promising route. Upgrading in aqueous phase is of particular interest because one could take advantage of the high water content of bio-oil. In terms of operation, a catalytic upgrading cascade process that includes several consecutive steps for different bio-oil fraction could be implemented. Biphasic systems represent a promising technical approach to achieve this goal, which operates on a continuous basis, involving multi-step reactions as well as product separation and removal.

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